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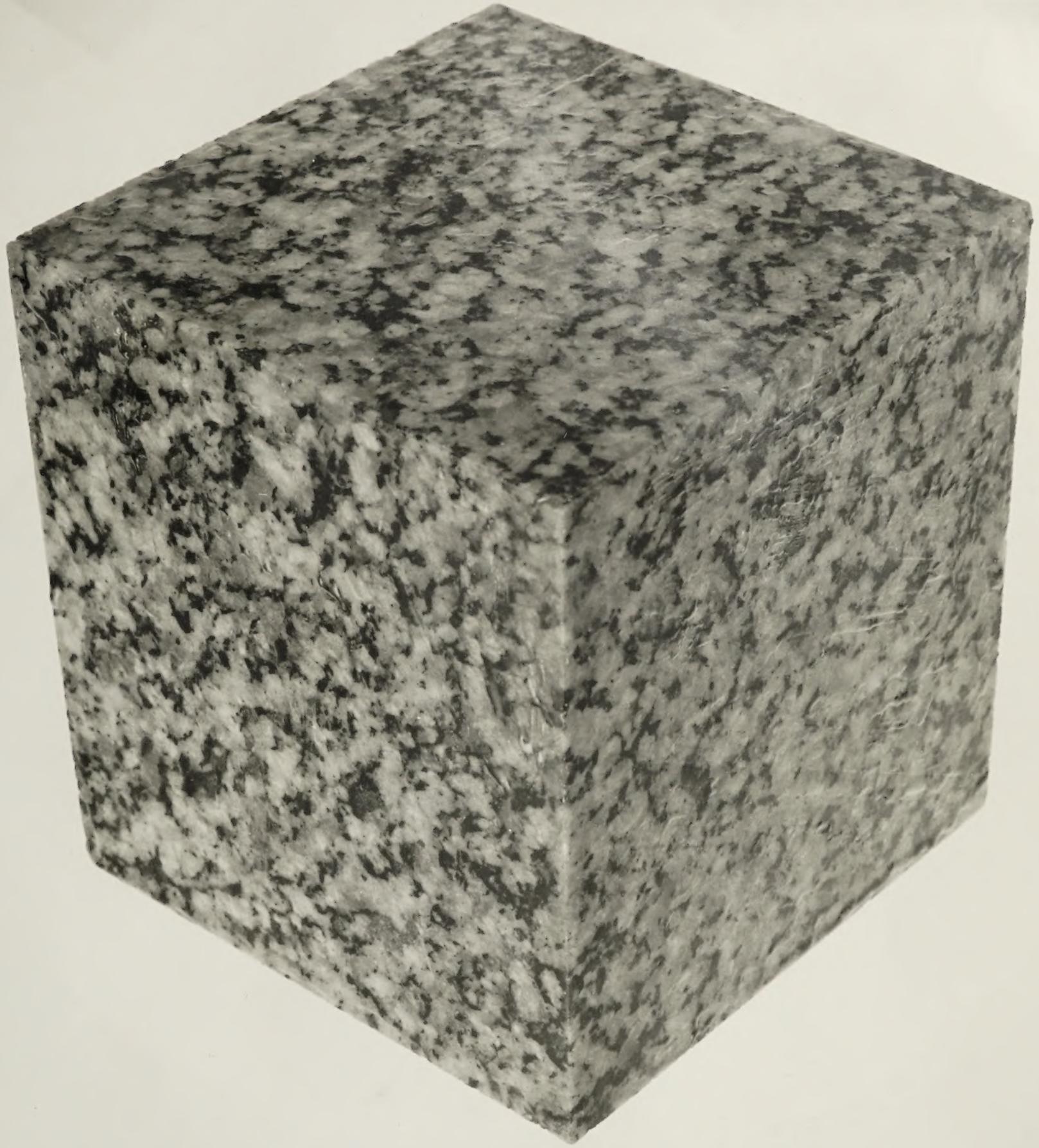
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True scale photograph of cut cube from the Southeast granodiorite, Yellowknife, N.W.T.

UNIVERSITY OF ALBERTA

THERMALLY INDUCED RELOCATION OF STRONTIUM AND RUBIDIUM IN A
GRANODIORITE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN PARTIAL
FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY

by

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UNIVERSITY OF ALBERTA

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Strontium has been relocated from granodiorite heated in air at 900°C for one week. In particular, a considerable proportion of the radioactive strontium was lost by leaching, while a comparatively small amount was gained by uptake. The significant increase in rubidium content is also discussed.

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Thermally Induced Relocation of Strontium and Rubidium in a Granodiorite", submitted by Otto van Breemen, in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Strontium has been relocated in a granodiorite heated in air at 900°C for two weeks. In particular, a considerable proportion of the radiogenic strontium was lost by biotite, while a comparatively small amount was gained by apatite. No significant amount of strontium was leached by water from the ground, heated rock sample. The radiogenic strontium lost by the biotite was possibly taken up by the plagioclase. The pattern of strontium relocation indicates that water has played an essential role in mobilizing the strontium ions.

An isochron plot of the unheated whole rock and minerals yields an age of $2,460 \pm 40$ m.y. with an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.701. A $2,390 \pm 50$ m.y. date on the biotite was obtained using the K-Ar technique. Loss of argon by the biotite during heating was greater than the corresponding loss of strontium.

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INTRODUCTION

Present knowledge of the movement and affinities of the parent and daughter isotopes of the Rb-Sr, K-Ar, and U-Th-Pb chronometers under varying conditions of temperature, pressure, and fluid media has been derived from geological case studies and from experimentation with individual minerals under controlled conditions of temperature, pressure, and fluid medium. Interpretation of isotopic relocation during metamorphism in natural cases depends on a knowledge of geological case histories. As the chronology of events are based partly on radiometric dates, circular arguments are difficult to avoid. Temperature and pressure conditions of metamorphism affecting these radiometric dates are not accurately known. Furthermore, considering the mobility of vapour and liquid phases and possibilities of metasomatism, one cannot be certain of dealing with a system of constant chemical composition throughout geological time. It is therefore usually difficult to interpret anomalous dates unequivocally. Studies of individual minerals have given specific information on the diffusion constants of rare gases at different temperatures and the effect of leach solutions on ionic isotopes.

Relative affinities, the presence of sinks, and the storage capacities at grain boundaries may be determined by experiments on multiphase rocks where a material balance is calculated. Such an experiment has been done on a gneiss-diorite by heating it in air at 900°C for a period of two weeks. This study is mainly a documentation of the movement of rubidium and strontium; in particular, radiogenic strontium (Sr^{87*}). Of major interest is the relative degree of loss of rubidium and strontium from various minerals under the conditions of the experiment. It is hoped that the findings in this thesis will be of some aid in interpretations of Rb-Sr dating.

CHAPTER ONE

MINERALOGY

1. Selection of sample

A fresh block of biotite granodiorite was collected on an island in Yellowknife Bay, Lat. $62^{\circ} 35' 41''$ N; Long. $114^{\circ} 16' 14''$ W, N.W.T. This sample was selected for the following reasons:

1. Certain essential minerals are present. Biotite and microcline are favourable minerals for Rb-Sr dating, and sufficient apatite is present to give the "initial" $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the rock. The high zircon content makes a comparative study of the U-Pb and Th-Pb systems possible.
2. The Archean age gives the rock a relatively high proportion of radiogenic Sr which makes the rock favourable analytically for the study of relative effects between normal and radiogenic strontium.
3. The rock is of a sufficiently small grain size to allow Rb and Sr to diffuse out of the grains while still making adequate mineral separation possible.
4. The sample is homogeneous. This is essential in order to assume constant composition for the heated and unheated blocks.
5. Enough sample has been collected in order to make possible an additive set of analyses of the rock heated to different temperatures.

2. Petrography

According to Moorhouse (1959) the rock is classified as granodiorite if the mode is used (Table 1) and sericitized plagioclase is included in the intermediate plagioclase. If sericite calculated from a chemical analysis is subtracted from the modal plagioclase, the rock is reclassified as quartz diorite.

The anorthite content of the plagioclase is found to be 26 percent using

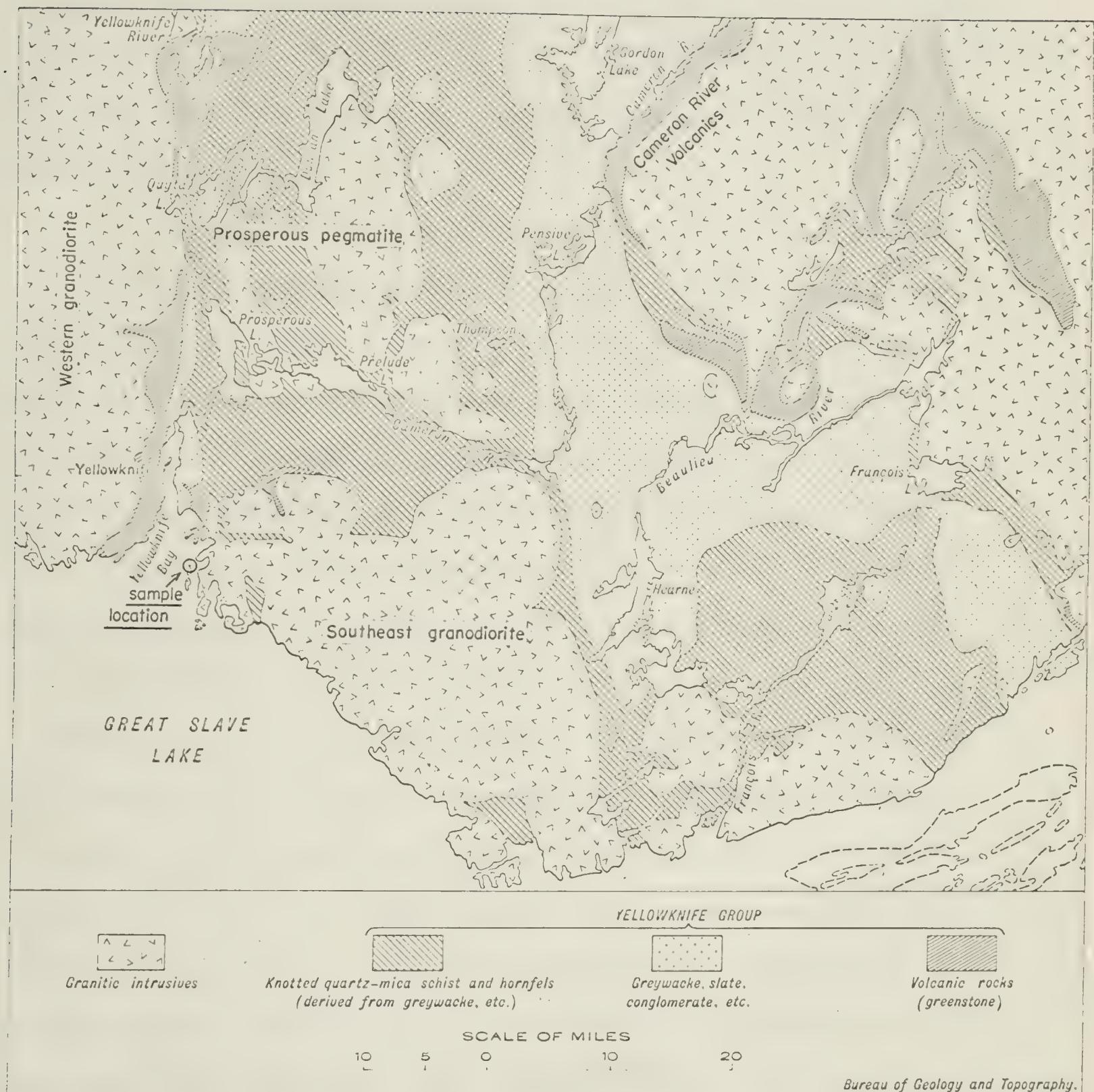


Figure 1. Index Map of the Yellowknife Area showing sample location.

the index of refraction. Some plagioclase crystals are zoned. No compositional variations within crystals could be determined. Approximately half the plagioclase shows sericitization. Sericite may be computed from the norm and makes up 21 wt. percent of the plagioclase.

Another alteration product, epidote, occurs as small crystals (predominantly in the sericitized parts of the plagioclase). This mineral is colourless and has $2V$ angles close to 90° . Distinction between epidote and clinozoisite is therefore not possible. Microcline shows characteristic grid-iron twinning and is distinguished from the twinning of anorthoclase by its greater extinction angle. No albite peaks were observed on an X-ray diffraction scan of the microcline.

Quartz showed undulatory extinction but no granulation. Biotite was almost completely unaltered. Chloritized biotite grains occurred, some of which had the blue birefringence colour of pennine. A few grains of green secondary hornblende were also observed with the biotite. Sphene occurred as tiny reddish brown grains within the biotite. A few grains (several millimeters in diameter) of a euhedral polygonal mineral could not be identified. The grains were mottled greenish brown in colour and had altered brown rims. Under crossed nicols the mineral appeared as a patchwork of isotropic segments of low birefringence. The metamict appearance plus the occurrence of radial fractures in the surrounding quartz suggested a radioactive mineral, possibly allanite.

Pyrite was observed, sometimes in association with the above undetermined mineral. Calcite occurred in tiny grains or veinlets. Zircon, which is abundant in this rock, occurred as euhedral crystals of the malacon variety. Where it is enclosed in biotite, radioactive haloes can be observed. Euhedral apatite prisms are abundant.

3. Modal analysis

For the purpose of material balance considerations, a modal analysis of the rock was carried out. In order to establish homogeneity throughout the block, eleven thin sections were cut. These were spaced 10 cm. apart on three perpendicular axes and cut at right angles to these axes. Compositional trends in three directions could thus be detected, if present.

Thin sections were cut to give a counting area of 600 sq. mm. On each section, 2700 point counts were made. Mineral percentages for eleven thin sections of the rock were listed in Table 1. Thin sections "x" were taken in numerical order from back to front, thin sections "y" were taken from left to right, and thin sections "z" were taken from bottom to top. No significant compositional trends could be observed. Consequently, the 10 cm. cubes within the block were taken to be of the same composition with a confidence error indicated by the standard deviations on the mineral determination of each thin section (Table 1).

A measure of coarseness of the rock was given by its I.C. number (Chayes, 1956). This was determined on each thin section by counting the number of major mineral changes over a length of 4 cm. An average I.C. number of 26.1 ± 4.8 for the rock was obtained. This indicates a relatively coarse-grained rock.

Chayes (1956) has calculated charts relating I.C. number, area of thin section, and number of thin sections with the major mineral analytical error for a homogeneous rock. The modal analysis of the rock should have given a value of the root of the variande less than 1.41. The larger standard deviations obtained from the modal analysis can be explained by the patchy distribution of the mafic and felsic minerals visible on cut surfaces.

TABLE 1

MODAL ANALYSIS ON ELEVEN THIN SECTIONS OF THE SOUTHEAST GRANODIORITE, YELLOWKNIFE, N.W.T.

	1 _x	2 _x	3 _x	4 _y	5 _y	6 _y	7 _z	8 _z	9 _z	10	11	Mean	S.D.
Quartz	29.13	26.34	25.43	25.54	33.45	29.48	24.11	31.78	22.92	30.28	33.83	28.39	3.76
Plag	28.64	26.92	25.70	26.56	26.83	27.38	19.56	23.08	29.31	26.46	23.55	25.82	2.79
Ser. Plag	30.00	27.47	32.31	26.93	24.53	24.44	30.93	30.27	28.12	26.79	23.47	27.75	2.89
Tot. Plag	58.64	54.39	58.01	53.49	51.36	51.82	50.49	53.35	57.27	53.25	47.02	53.57	3.48
Biotite	7.68	15.50	13.49	14.50	11.75	14.46	19.94	11.31	15.64	11.33	14.71	13.67	3.16
Microcline	2.95	1.67	1.40	4.15	1.68	2.72	3.18	1.85	1.74	4.26	2.73	2.58	1.00
Zircon	.00	.12	.00	.03	.04	.04	.15	.08	.08	.07	.08	.06	.05
Apatite	.15	.43	.11	.24	.15	.27	.34	.26	.28	.18	.08	.23	.10
Sphene	.34	.62	.49	.72	.54	.50	.72	.45	.52	.26	.46	.51	.14
Clinozosite	.53	.58	.34	.75	.77	.42	.61	.68	.60	.18	.46	.54	.17
Calcite	.15	.12	.38	.03	.19	.19	.23	.15	.12	.07	.00	.15	.10
Pyrite	.00	.04	.00	.10	.00	.00	.04	.04	.00	.00	.00	.02	.03
Chlorite	.08	.08	.04	.37	.08	.04	.11	.04	.20	.07	.04	.10	.10
Unknown	.34	.12	.23	.07	.00	.08	.08	.00	.44	.04	.61	.18	.28
TOTAL	99.99	100.01	100.00	99.99	100.01	100.02	100.00	99.99	100.03	99.99	100.02	100.01	

4. Norm Calculations

The rock was carefully analysed by standard wet chemical procedures, and a C.I.P.W. norm and a mesonorm (Barth 1962) calculated (Table 2). A differentiation index (Thornton and Tuttle, 1960) calculation for the rock yields a value of 74.8.

TABLE 2

CHEMICAL ANALYSIS AND NORMS OF THE GRANODIORITE OF THE SOUTHEAST GRANODIORITE, YELLOKNIFE, N.W.T.

Chemical Analysis		C.I.P.W. Norm		Mesonorm	
SiO ₂	65.90	Quartz	22.31	Quartz	23.67
Al ₂ O ₃	16.34	Orthoclase	18.14	Orthoclase	11.55
Fe ₂ O ₃	.44	Albite	34.42	Albite	36.60
FeO	4.01	Anorthite	12.14	Anorthite	11.15
MnO	.04	Hypersthene	10.21	Biotite	12.40
MgO	1.18	Hematite	.37	Magnetite	.53
CaO	2.87	Ilmenite	.85	Sphene	1.08
Na ₂ O	4.00	Apatite	.49	Apatite	.51
K ₂ O	3.20	Corundum	1.06	Corundum	2.51
TiO ₂	.51	Total	99.99	Total	100.00
P ₂ O ₅	.24				
H ₂ O	.06				
H ₂ O ⁺	1.08			Analyst - O. van Breemen	
Total	99.87				

This value places the rock between granite (D.I. = 80) and granodiorite (D.I. = 67) in "basicity". On plotting the rock on Thornton and Tuttle's (1960) contour diagrams of the distribution of the consecutive oxides (Al₂O₃, Fe₂O₃, CaO, MgO, FeO, K₂O, and Na₂O of the 5,000 analyses of Washington's Tables (Washington 1917) as a function

of the differentiation index, the rock was found to be of a common igneous composition. The experiment was thus carried out on a representative igneous rock.

The mesonorm as suggested by Barth is more realistic than the C.I.P.W. norm as it accounts for the biotite. However, it fails to consider the sericitization of plagioclase. The excess potassium is thus calculated as orthoclase and makes the K-feldspar content too large.

In order to make a realistic appraisal of the consistency between the chemical analysis and the modal mineral composition, a norm has been calculated which is based on the mesonorm of Barth but which has the following deviations (Table 3):

1. Minor minerals (pyrite, calcite, zircon, and clinozoisite) not taken into account by the mesonorm calculation were taken from the mode and their cation percentages were subtracted from the total.
2. As Ti can substitute for Al in biotite, the same was done for sphene.
3. No magnetite was calculated as it did not appear in the rock.
4. The trivalent cation in biotite was made up of the remaining Ti, all Fe'', and Al.
5. A stoichiometric amount of (OH) was calculated for biotite, clinozoisite, and apatite. The remainder was used to calculate sericite.
6. Potassium cationic percentages for biotite and sericite were summed and subtracted from the total to calculate microcline.
7. Major and minor mineral cation percentage were converted to volume percentages from molar volumes per 100 cations as listed by Barth (1955).

With the exception of biotite, chemical formulas used in the calculation of the mesonorm were adopted. Formulas used for biotite and for minerals not represented in the mesonorm are given in Table 4.

TABLE 3

CALCULATION OF MODAL MINERAL PERCENTAGES FROM CHEMICAL ANALYSIS

	Cat %	Pyr	Ti	Calc	Zir	Clin	Ap	Ab	An	Bi	Ser	Micr	Q	C
Si	62.03		.17		.03	.20			21.96	4.26	4.84	5.19	1.56	23.82
Ti	.36		.17							.19				
Al	18.15					.20			7.32	4.26	1.10	5.19	.52	-.44
Fe ^{II}	.32									.32				
Fe ^{II}	3.17		.02								3.15			
Mn	.03										.03			
Mg	1.66											1.66		
Ca	2.91					.17	.15		.14	.32		2.13		
Na										7.32				
K	3.86											1.61	1.73	.52
P												.19		
(OH)	(6.81)								(.07)	(.06)		(3.22)	(3.46)	
Total	100.00		.02	.51	.15	.03	.54		.51	36.60	10.65	12.90	12.11	2.60
Mol. Vol. per 100 cat. ($\times 1/10 \text{ cm}^3$)										200	200	190	202	218
Vol. Prop.												7320	2130	2451
Vol. %													567	5383
												35.59	10.35	11.91
													2.76	26.18

TABLE 4

CHEMICAL FORMULAS USED FOR CALCULATING MINERAL COMPOSITION FROM CHEMICAL COMPOSITION

Biotite	$K(Mg, Mn, Fe'')_3 (Al, Ti, Fe''') Si_3O_{10}(OH)_2$
Sericite	$KAl_3Si_3O_{10}(OH)_2$
Clinzozoisite	$Ca_2Al_3(SiO_4)_3(OH)$
Zircon	$ZrSiO_4$
Calcite	$CaCO_3$

Percentages of major and minor minerals calculated from the chemical analysis are compared in Table 5. Quartz, biotite, and microcline percentages agree within one standard deviation of the modal analysis. The plagioclase plus sericite content agrees within two standard deviations. Plagioclase calculated from the chemical analysis has an anorthite content of 22.5 mol. percent. This compares to an anorthite content of 26 mol. percent determined by the Becke line method.

TABLE 5

COMPARISON OF MINERAL PERCENTAGES OF THE GRANODIORITE CALCULATED FROM THE CHEMICAL ANALYSIS WITH THE MODE

<u>Mineral</u>	<u>Mode</u>	<u>Volume Percentages Calculated from the Chemical Analysis</u>
Quartz	28.39 ± 3.76	26.18
Plagioclase & Sericite	53.57 ± 3.48	57.83
Biotite	13.67 ± 3.16	11.91
Microcline	2.58 ± 1.00	2.76

The errors in the chemical analysis and the assumptions in the mineral calculation are difficult to assess. The mineral comparisons would suggest that the errors in the norm are of the same magnitude as the statistical errors in the mode.

As Chayes' charts show that the error in the modal analysis is due to the inhomogeneity of the rock rather than grain size, it is not likely that the statistical error can be improved. However, considering the limitations on the material balance calculations caused by the difficulties in obtaining representative mineral separates, the accuracy of this modal analysis is adequate.

As the mode is a more direct approach and therefore less liable to bias, the modal mineral composition is preferable. The norm should be used only for minerals indistinguishable in thin section. The agreement between the mode and the norm indicates that the calculation of sericite from the norm was correct.

CHAPTER TWO

HEATING AND ANALYSIS

1. Preparation of heated and unheated samples

Four 10-cm. cubes were cut from the granodiorite boulder. Rock slices spaced regularly through the boulder were selected for an unheated whole rock sample. These slices were pulverized with a Plattner mortar, ground in an agate mortar, and thoroughly homogenized on paper.

One of the cubes was heated to 900°C in an oven for fourteen days. This rock was heated gradually up to 900°C in 27 hours. As not enough apatite and zircon could be obtained from the first heated block, a second block was heated for the same length of time. This time the temperature was taken up to 900°C in approximately five hours.

All the mineral separates were obtained from the first heated block with the exception of part of the apatite and zircon. A fraction of the quickly heated rock was taken for the purpose of leaching.

2. Changes in the Heated Sample

Both heated blocks were permeated by a continuous network of fractures. The rock was thus extremely friable and could be pulverized with ease.

The biotite had turned reddish brown, indicating that the iron had oxidized. Penfield tube analyses showed that the unheated biotite contained 3.76% water, all of which was lost on heating.

In the gradually heated rock, a considerable amount of iron had moved out of the biotite showing up as yellow concentrations of iron oxide adjacent to the biotite and extending into the network of fissures through the rock. In the quickly heated rock this yellow iron oxide did not appear, suggesting that the

movement of iron out of the biotite is related to the rate at which water is driven from the biotite lattice.

A thin section was made of the quickly heated rock after it was impregnated with "Plastiglo". It was found that the fractures passed through crystals and only showed a slight preference for grain boundaries. Consequently, most minerals were left in contact.

In spite of a mask of red iron oxide, the heated biotite showed pleochroism and parallel extinction; indicating that its structure was retained. According to Roy (1949), biotite retains its structure on heating until 1100°C. It is inferred that with the loss of water and oxidation of iron, oxy-biotite was formed.

The fine indistinguishable sericite appeared to have broken down as it had formed a fibrous isotropic mat, masking the birefringence of the plagioclase. Many of the larger distinct sericite flakes had retained their optical properties, showing muscovite birefringence and parallel extinction. This phenomenon could be in keeping with Roy's (1949) findings according to which muscovite does not show any marked structural change until 940°C. As the breakdown temperature is approached, it is conceivable that the sericite reacted with the stable plagioclase. Such a reaction would be expected to proceed faster with the finer sericite, thereby explaining the apparent structural breakdown of the finer sericite while the coarser flakes remained relatively unchanged.

3. Mineral Separation and Sample Preparation

Both heated and unheated rocks were ground by a Brown rock crusher. The ground rock was separated into heavies, a felsic concentrate, and a biotite concentrate on a Wilfley table. Rough felsic and biotite purifications were made by allowing the sample to fall between the two vertically tilted magnets of a Frantz isodynamic separator and collecting two magnetically separated streams.

The biotite was purified further using the Frantz isodynamic separator, felsics were floated off in tetrabromoethane and heavies were sunk in methylene iodide.

As inclusions of sphene and apatite could greatly affect the strontium analysis, fine samples of heated and unheated biotite were used for the Rb-Sr analysis. An 80-150 mesh fraction was taken for the unheated biotite and a 115-250 mesh fraction was taken for the heated biotite. These size fractions were roughly equivalent as the heated biotite did not cleave into thin flakes. Poorer cleavage of the heated biotite resulted in a less complete removal of inclusions. Iron oxide from the biotite included other impurities, making it impossible to obtain a pure heated phase. Consequently whole rock contamination in the order of one percent could easily be present.

Unheated microcline, quartz, and plagioclase were separated from the felsic fraction using mixtures of tetrabromoethane and acetone in varying proportions. Unheated plagioclase could not be separated into its pure and sericitized components as these were of the same specific gravity. Through the loss of water from sericite, the heated sericitized plagioclase was lighter than the pure phase so that a separation could be made. Specific gravities for the heated sericitized plagioclase overlapped those of quartz and microcline. A sample of microcline was handpicked. This separate was contaminated by sericitized plagioclase.

The heavy minerals were purified by floating off the felsics in tetrabromoethane. The apatite was separated by floating it in methylene iodide. The nonmagnetic fraction on the Frantz magnetic separator was taken at a tilt of 5° and an amperage of 1.5 amps. As many of the heated apatite crystals were covered with iron oxide from the biotite, a considerable fraction of the heated apatite was lost during the magnetic separation.

All mineral separates were washed with demineralized water. A leach

was obtained from the heated whole-rock fraction. A sample weighing 143.9 gm was immersed in 100 cc of water at room temperature for three days.

4. Reagents and apparatus

Azeotropes of hydrochloric and nitric acids used in the chemical breakdown of the samples were redistilled in a fused quartz distillation flask. All water was distilled and demineralized.

Teflon beakers were used for the hydrofluoric acid breakdown of the samples. Otherwise pyrex glassware was used. The teflon beakers, stirring rods, cover lids, and all glassware was scrubbed with detergent in hot water, rinsed with demineralized water, immersed in hot one to one hydrochloric acid for three hours and rinsed with demineralized water. Clean glass beakers and centrifuge tubes were wrapped in "Parafilm" and stored for use.

5. Chemical Procedure

X-ray fluorescence assays were done on the whole rock and individual minerals. The optimum amounts of sample to be mixed with strontium and rubidium spikes were calculated from these approximate strontium and rubidium concentrations. Quarter gram samples were broken down with hydrofluoric and nitric acid and taken up in dilute HC1. Aliquots containing the calculated sample amounts for spiking were mixed with the strontium and rubidium spikes. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the sample was measured on the remaining solution. Strontium was separated by Dowex-50-X8 ion exchange columns and evaporated down as a perchlorate. The rubidium fractions were converted to sulfates. Blanks were determined for strontium and rubidium using the same amount of reagents as in the sample analysis.

6. Mass Spectrometry

The mass spectrometer employed was a solid source, single filament instrument with a 60°-sector magnetic deflection. Tantalum filaments were used. Strontium was loaded in the form of a perchlorate and converted to an oxide on the filament. Rubidium was loaded in the form of a sulfate.

CHAPTER THREE

RESULTS AND DISCUSSION

1. The isochron plot

The strontium and rubidium data for the whole rock and both heated and unheated minerals has been graphically displayed by an isochron plot of the type suggested by Nicolaysen (1961). An example of this type of plot is shown in Figure 2 for a rock with four analyzed minerals.

For a rock that has undergone no metamorphism or alteration since crystallization, the whole rock and mineral points will fall on a straight line or isochron. The equation for this isochron is derived from the expression giving the Sr^{87} content of a sample at time "t" after it became an isolated system, in terms of the initial Sr^{87} content, the decay constant, λ , and the Rb^{87} content at time "t":

$$\text{Sr}_{\text{t}}^{87} = \text{Sr}_{\text{i}}^{87} + \text{Rb}_{\text{t}}^{87} (e^{\lambda t} - 1)$$

dividing by the Sr^{87} content (Sr^{86} content is non radiogenic and assumed constant).

$$\frac{(\text{Sr}^{87})}{(\text{Sr}^{86})_{\text{t}}} = \frac{(\text{Sr}^{87})}{(\text{Sr}^{86})_{\text{i}}} + \frac{(\text{Rb}^{87})}{(\text{Sr}^{86})_{\text{t}}} (e^{\lambda t} - 1)$$

An isochron date can be calculated from the slope. The zero intercept gives the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio for the rock.

Experimentally induced isotopic movements are shown by deviations of the heated minerals from the isochron. Trends toward homogenization are indicated by a movement of the mineral points toward a horizontal zero isochron passing through the whole rock point.

2. Results

The results of the strontium and rubidium isotopic analyses are given in

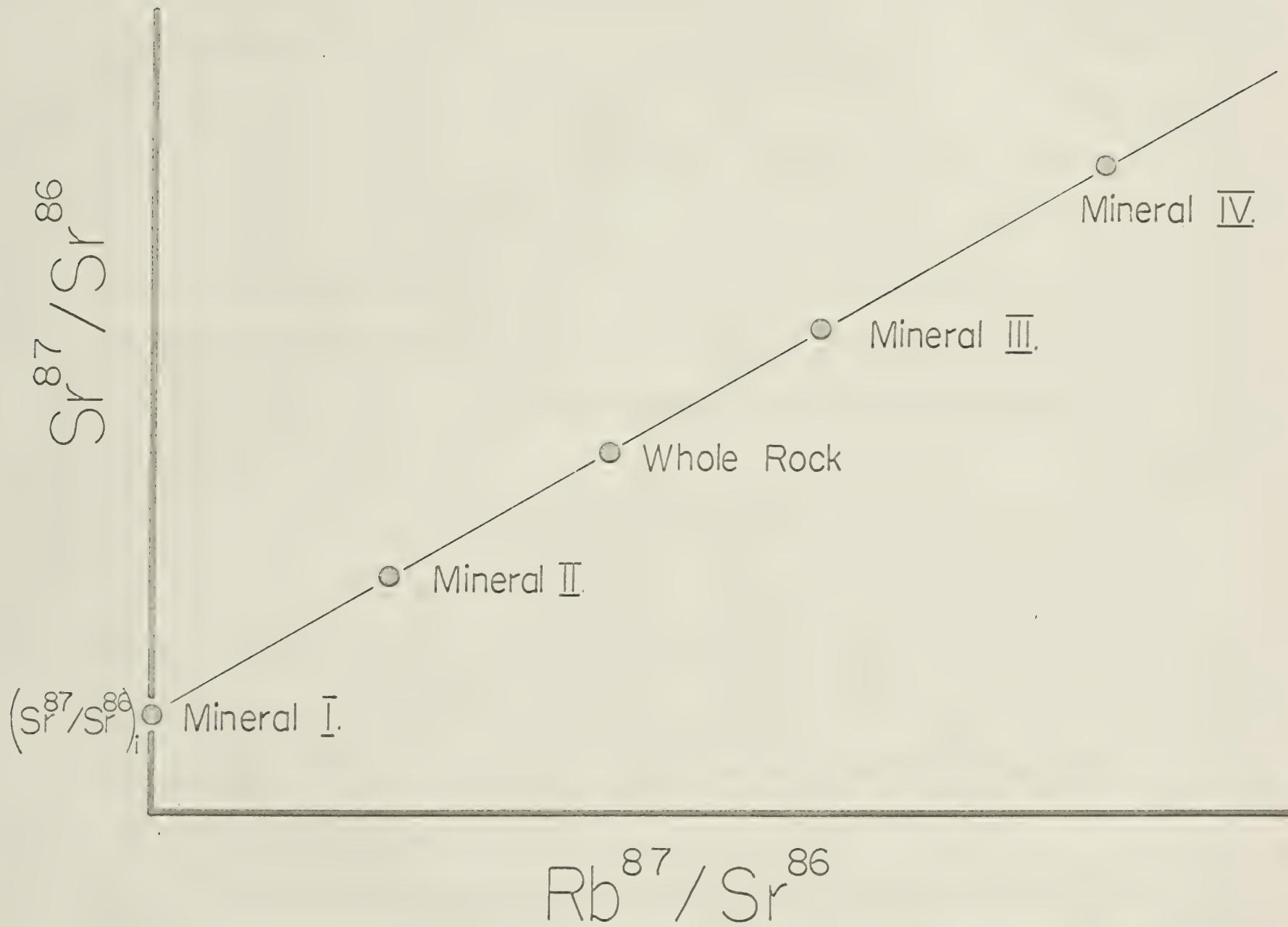


Figure 2. Whole rock and mineral isochron plot.

Table 6. The errors are precision errors on the complete isotopic analyses within one to two standard errors (Analytical precision and accuracy are discussed in the appendix). A value 1.47×10^{-11} /yr. has been adopted for the decay constant, λ , of Rb⁸⁷ (Flynn and Glendenin, 1960).

Figure 3 shows the plot of Sr⁸⁷/Sr⁸⁶ versus the Rb⁸⁷/Sr⁸⁶ ratios for the unheated whole rock and minerals and the heated minerals. A $2,460 \pm 40$ m.y. isochron has been fitted to the plots of the unheated whole rock and mineral phases. The isochron intercepts the vertical axis at the initial Sr⁸⁷/Sr⁸⁶ ratio of $0.701 \pm .001$. Errors on the age and the initial Sr⁸⁷/Sr⁸⁶ ratio are discussed in the appendix.

The low initial Sr⁸⁷/Sr⁸⁶ ratio suggests that the granodiorite was derived from a source having a Rb/Sr ratio similar to the source regions of basalts shortly before it was emplaced (Hedge and Walthall, 1963). The concordancy of the isochron plot indicates that the rock experienced no movement of strontium or rubidium after crystallization.

Potassium-argon analyses have been run on the 35-60 mesh size fraction of the heated and unheated biotite (Table 7). The K-Ar date of 2,390 m.y. on the unheated biotite compares to the isochron date within analytical error if a ± 2 percent analytical error is taken for the K-Ar analysis. K⁴⁰ decay constants of $\lambda_c = 0.589 \times 10^{-10}$ /yr, and a 0.0119 atomic percent normal K⁴⁰ content and $\lambda\beta = 4.76 \times 10^{-10}$ /yr. were adopted.

The 93 percent loss of argon from the biotite is reasonable as the diffusion of argon is not limited by chemical bonding. The apparent loss of potassium is inexplicable as no apparent corresponding loss of the diadothic rubidium was observed. The potassium determination on the heated biotite has to be confirmed.

The pattern of strontium movement is similar to that observed in nature. Radiogenic strontium has been lost by the biotite and gained by the apatite and possibly the plagioclase, both strontium-bearing minerals.

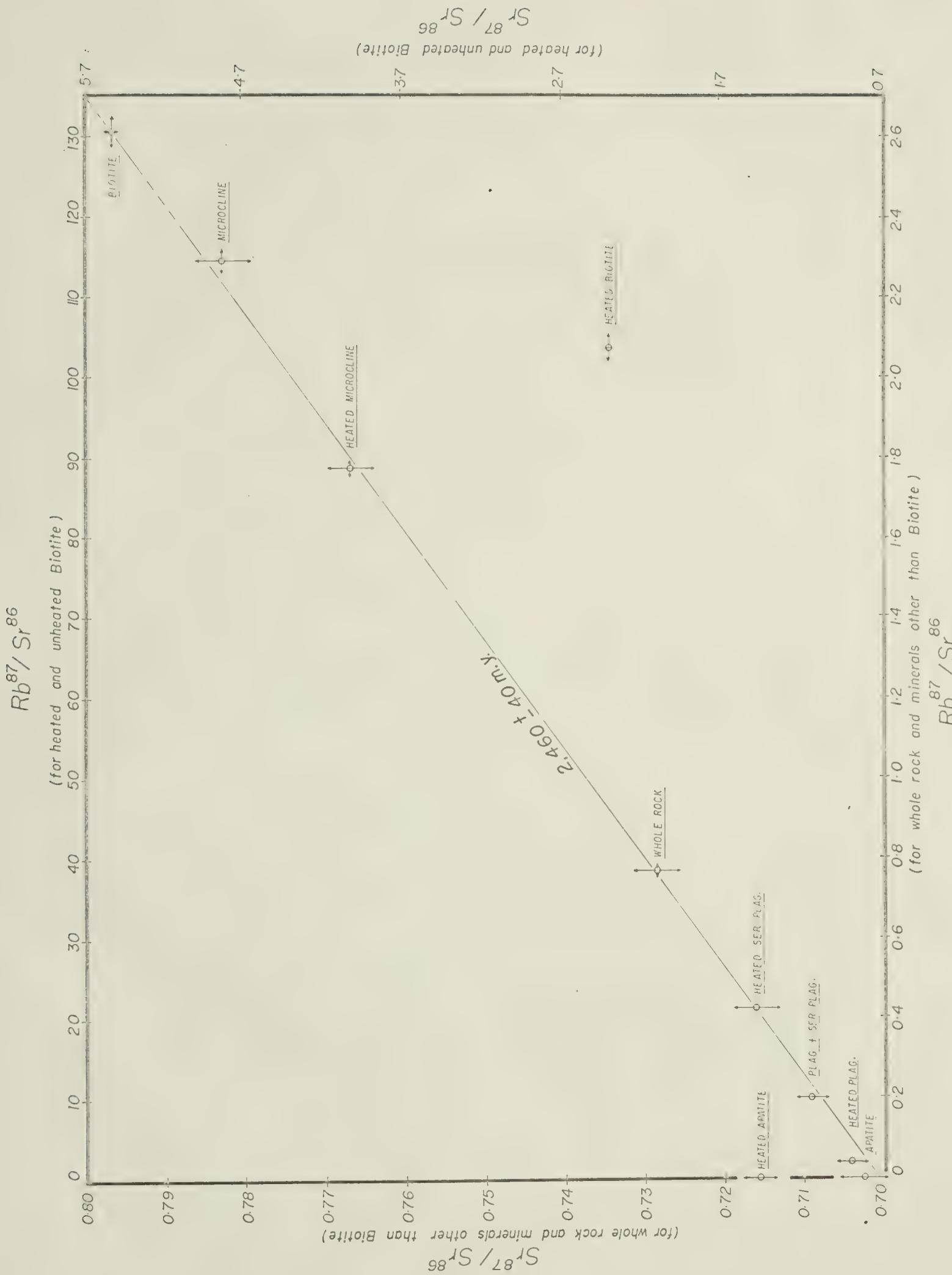


TABLE 6

STRONTIUM AND RUBIDIUM ANALYTICAL DATA FOR THE SOUTHEAST GRANODIORITE,
YELLOWKNIFE, N.W.T.

	Sr ⁱ ppm	Sr ^{87*} ppm	Sr [†] ppm	Rb ppm	Sr ⁸⁷ /Sr ⁸⁶	Sr ⁸⁷ /Sr ⁸⁶
Whole rock	308.5 ± 6.9	0.81 ± .50	309.3 ± 6.9	82.0 ± .95	0.7285 ± .003	0.769 ± .020
Biotite	8.61 ± .076	3.95 ± .048	12.56 ± .090	388.1 ± 5.5	5.51 ± .03	130.5 ± 2.2
Biotite Heated 115-250 M	10.45 ± .086	1.96 ± .020	12.41 ± .087	382.5 ± 5.4	2.381 ± .008	103.7 ± 1.8
Microcline	154.89 ± .69	1.25 ± .075	156.14 ± .69	122.5 ± 1.5	0.783 ± .0035	2.287 ± .031
Microcline Heated	230.2 ± 1.3	1.85 ± .12	232.00 ± 1.3	141.2 ± 1.7	0.767 ± .003	1.773 ± .022
Plagioclase and Ser Plag.	535.5 ± 2.6	0.43 ± .21	535.97 ± 2.6	37.25 ± .45	0.709 ± .002	0.201 ± .0027
Plagioclase Heated	529.4 ± 2.8	0.18 ± .20	529.60 ± 2.8	7.19 ± .085	0.704 ± .003	0.0393 ± .0005
Ser Plag. Heated	590.8 ± 3.4	0.89 ± .25	591.64 ± 3.4	87.0 ± 1.1	0.716 ± .003	0.426 ± .006
Apatite	193.0 ± 2.2	.03 ± .16	193.06 ± 2.2		0.7025 ± .003	
Apatite Heated	188.1 ± 2.5	.27 ± .18	188.36 ± 2.5		0.7155 ± .002	
Leach Heated Rock	0.000915 ± ,000031 -	.000035 ± ,00008 -		.000950 ± ,000032 -	1.09 ± .093	

TABLE 7
K-Ar DATA ON THE UNHEATED AND HEATED
BIOTITES

	Ar ppm	K ₂ O %	Date m.y.
Unheated Biotite	2.511	8.82	2,390
Heated Biotite	.1785	6.18	436

The loss of radiogenic strontium is real as the biotite has such a high content of radiogenic strontium that the isotopic determination could only be slightly affected by impurities in the sample. This loss cannot be quantitatively accounted for by the gain of radiogenic strontium in the apatite. The analysis of the leach indicates that only a negligible amount of strontium moved into the fractures, most compounds of strontium being sufficiently soluble to have been taken up by the leach.

An alternative explanation is that the radiogenic strontium lost by the biotite was gained by the plagioclase but that the increase of radiogenic strontium in plagioclase was not measurable within the experimental error. As no equivalent phases of the heated and unheated plagioclase have been obtained, the plausibility of the above explanation can only be verified on the basis of the deviation of the probable precision error on the Sr⁸⁷/Sr⁸⁶ ratio of the unsericitized plagioclase plus differences in this ratio from the isochron plot in the direction of increasing Sr⁸⁷/Sr⁸⁶ ratio. A loss of 1.99 ppm radiogenic strontium from the biotite would result in a corresponding increase in the Sr⁸⁷/Sr⁸⁶ ratios of the plagioclase and

sericitized plagioclase of 0.0073 which is double the increase that could be accounted for by the precision of measurement and the deviation of the ratios from the isochron.

The 35-60 mesh fraction of the heated biotite gives a $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 4.31. The greater ratio for the larger mesh size indicates that strontium loss from the larger biotite flakes was less extensive than for the smaller flakes. It is assumed that since the granodiorite has not undergone isotopic movements after crystallization, the Sr and Rb isotopic content and composition of the unheated biotite is the same for all grain sizes. As a large portion of the biotite in the crushed heated rock is coarser than 115 mesh, the amount of radiogenic strontium loss by the biotite will be considerably less than the amount calculated above. Accordingly the increase in the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of the plagioclase and the sericitized plagioclase is less and could be within the precision error.

The apparent gain of 1.84 ppm initial strontium by the biotite can be accounted for by less than one percent whole rock contamination. As impurities in the heated biotite could easily amount to one percent, the measured increase in initial strontium is not considered real (see Mineral separation).

A higher initial strontium content is shown for the heated sericitized plagioclase than for the heated plagioclase. The centers of the plagioclase crystals are sericitized more extensively than the rims. As zoning was apparent, the centers of the plagioclase crystals should be richer in anorthite and thus show an increase in strontium.

The heated microcline has moved down along the isochron as a result of incomplete separation from the heated sericitized plagioclase. The increase in rubidium and radiogenic strontium can be explained by the fact that only heated plagioclase with a very high content of sericite had been reduced

sufficiently in specific gravity through the loss of water to attain the same specific gravity as the microcline. This made gravity separation impossible.

3. Rubidium and Strontium balance considerations

Contributions of original strontium, radiogenic strontium and rubidium of both heated and unheated minerals to the whole rock were calculated. Sums of the unheated and heated minerals were compared to the whole rock composition to determine whether all strontium and rubidium has been accounted for in the mineral phases (Table 8). Average specific gravities for the minerals were taken from the Handbook of Chemistry and Physics (1960). The specific gravity of the whole rock was determined with a quartz glass pycnometer.

As a pure heated microcline phase could not be obtained, strontium and rubidium contents for heated and unheated microcline were assumed to be the same. The unheated plagioclase plus sericitized plagioclase were taken to represent the average altered plagioclase. The heated plagioclase and sericitized plagioclase were assumed to be equivalent to the plagioclase and sericitized plagioclase phases of the modal analysis.

Since the error in the last two assumptions could not be determined, the agreement between the sum of the strontium content of the minerals and the whole rock strontium content could not be checked accurately. The discrepancy for the radiogenic content of the heated minerals, however, was believed to be the result of the variations in the isotopic composition of the different heated biotite grain sizes.

TABLE 8

MATERIAL BALANCE FOR STRONTIUM AND RUBIDIUM IN THE SOUTHEAST GRANODIORITE, YELLOWKNIFE, N.W.T.

	Volume percent	Specific gravity	Weight percent	Sr^{+} ppm	Sr^{87*} ppm	Initial Sr contribution	Radiogenic Sr contribution	Rb contribution
Unheated Granodiorite								
Plag. & Ser. Plag.	53.57	2.65	52.66	535.5	0.43	282.0	.23	37.25
Biotite	13.67	3.00	15.20	8.61	3.95	1.3	.60	388.1
Microcline	2.58	2.555	2.44	154.9	1.25	3.8	.03	122.5
Apatite	.03	3.20	.27	193.0	.03	.5	—	3.0
TOTAL						287.6	.86	81.6
Heated Granodiorite								
Plag.	25.82	2.65	25.38	529.4	0.18	134.4	.05	7.19
Ser. Plag.	27.75	2.65	27.28	590.8	0.89	161.1	.24	87.0
Biotite	13.67	3.00	15.20	10.45	1.96	1.6	.30	382.5
Microcline	2.58	2.555	2.44	154.9	1.25	3.8	.03	122.5
Apatite	.23	3.20	.27	188.1	.27	.5	—	3.0
TOTAL								86.6
Whole Rock		2.697						82.0

4. Speculations

Whereas on release from its lattice position, argon moves out of a mineral by simple volume diffusion, the movement of strontium is restricted by chemical bonding. Bowen has pointed out that ionic diffusion is insignificant until a mineral approaches its melting point. Both biotite and apatite melt at temperatures considerably higher than 900°C. This factor, combined with the geologically-short time of heating, makes it unlikely that ionic diffusion has played a significant role in the documented movement of the strontium.

The only plausible alternative is that water has provided an effective medium for transportation. The loss of iron from the slowly heated biotite which has not been observed for the quickly heated biotite suggests that only when the water in the biotite was driven off slowly did the iron have sufficient time to migrate out of the lattice. The role of water is also suggested by the association between the loss of radiogenic strontium and the loss of water from the biotite. Minor endothermic peaks at 800°C, corresponding to the loss of hydroxyl have been observed for the d.t.a. curves of apatite (Silverman et al., 1953). Thus water may also have been essential to the gain of radiogenic strontium by the apatite.

According to Gerling and Morozova (1962), the argon in micas need to overcome only the energy barrier of the oxygen atoms in the potassium layer, after which it diffuses readily along the cleavage plane. Khudsaidze (1962) found that the oxidation of ferrous iron in biotite increases the diffusion rate of argon in the temperature interval of 700° to 900°C. He also found that the diffusion of argon from different size fractions of biotite heated in air is the same. It thus appears that during the expulsion of hydroxyl and the oxidation of the iron, the octahedral layer of biotite offers little lattice resistance to the migration of argon atoms. As it is likely that water was essential to the movement

of the strontium ions, it is reasonable to assume that after release from the potassium layer, the radiogenic strontium moved along the cleavage planes in a medium of water.

A considerable portion of the water in the sericitized plagioclase was lost, showing that water has moved through the plagioclase lattice during the heating of the rock. Experimental and geological evidence shows that the intergranular network of rocks offers far less resistance to passing solutions and vapours than the mineral lattices (Ramberg, 1952). It is further reasonable to assume that as a result of differences in the thermal coefficients of expansion between the minerals, submicroscopic fractures along the mineral boundaries have formed.

One may reason that the water, on leaving the cleavage planes of the biotite, has moved along the grain boundaries to the visible cracks. If the plagioclase has gained radiogenic strontium, one should picture the ionic movement of individual strontium ions from the grain boundaries into the plagioclase lattice rather than strontium being carried along by water vapour passing through the plagioclase lattice. This interpretation implies that the radiogenic strontium from the biotite did not reach the apatite in the plagioclase grains. Accordingly, only the apatite inclusions in the biotite could have gained radiogenic strontium.

5. Summary

This experiment has shown that by heating in air it is possible to relocate strontium in a rock containing hydrous phases. It appears likely that water plays an essential role in the movement of strontium ions.

In particular, biotite has shown a clear inability to retain radiogenic Sr^{87} at high temperatures. This is attributed to the expulsion of water and the fact that the mica lattice is a poor host to strontium. The greater proportional loss of argon compared to radiogenic strontium suggests that simple heating of

biotite in the absence of external solutions has a greater effect on the K-Ar than on the Rb-Sr dating system.

As it is unlikely that the water from the biotite passed through the lattices of the apatite crystals, the gain of radiogenic strontium by the apatite shows that water can act as a medium for the movement of strontium ions as opposed to being a simple "effluent" carrier.

Thermal diffusion of strontium to or from feldspar was not measureable under the conditions of this experiment.

The granodiorite is 2,460 m.y. old on the basis of the isochron plot. Little or no significant chemical alteration has occurred since the time of its emplacement. An initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.701 suggests a source with a Rb/Sr ratio similar to the source regions of basalts.

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APPENDIX

Discussion of Errors

Since for all the analyses quarter gram samples were used, errors in weighing and in homogeneity of the samples were considered negligible. The main source of error was in the precision of the rubidium and strontium isotopic ratio measurements. As a result of a poor calibration run, the error for the weight and composition of a strontium spike was also significant (Table 9).

TABLE 9
SPIKE SET NO. 2

spike weight	= 3.956 \pm .015 ug
Sr ⁸⁶ weight fraction	= 0.5995 \pm .00065
Sr ⁸⁸ weight fraction	= 0.1231 \pm .00065

A smaller error on a more accurately calibrated strontium spike used for the leach was calculated to be negligible.

Errors on measured isotopic ratios and their combined contributions to the errors in the weights of rubidium and strontium were listed in Table 10. Poor emission made it impossible to devise a scheme for the satisfactory determination of standard errors of the means of the isotopic ratios. Errors, one to two standard errors in magnitude were estimated from the standard deviation within sets of peak measurements and the reproducibility of the means of these sets. For the unspiked strontium, the Sr⁸⁷/Sr⁸⁶ ratio was normalized to the accepted value of Sr⁸⁶/Sr⁸⁸ = 0.1194 for each set. The error was then estimated from the standard deviations of both the ratios in each set and the reproducibility of the normalized Sr⁸⁷/Sr⁸⁶ ratio between sets.

The Rb⁸⁵/Rb⁸⁷ ratio could not be corrected for mass discrimination by the simultaneous measurement of known potassium isotopic ratios (Jager, 1964).

TABLE 10

ANALYTICAL DATA

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Sample	$(\text{Sr}^{88}/\text{Sr}^{86})$ meas. S.E.	$(\text{Sr}^{84}/\text{Sr}^{86})$ meas. S.E.	$(\text{Sr}^{88}/\text{Sr}^{86})$ corr. S.E.	Sr^{88} N_{ug} S.E.	$(\text{Sr}^{87}/\text{Sr}^{86})$ corr. S.E.	$(\text{Rb}^{85}/\text{Sr}^{87})$ meas. S.E.	Rb^{85} + 5.5 S.E.
Whole Rock	1.865 + .02 -	0.3334 + .003 -	1.845 + .027 -	5.37 + .12 -	0.7285 + .003 -	0.281 + .0028 -	1.264 + .015 -
Biotite	0.692 + .003 -	0.3880 + .002 -	0.692 + .0033 -	1.365 + .012 -	5.51 + .03 -	0.737 + .0074 -	4.191 + .059 -
Biotite Heated	0.918 + .003 -	0.380 + .003 -	0.925 + .0041 -	2.074 + .017 -	2.381 + .0069 -	0.755 + .0076 -	4.345 + .062 -
Microcline	2.223 + .004 -	0.3254 + .0005 -	2.268 + .0042 -	8.094 + .036 -	0.783 + .0035 -	0.469 + .0047 -	1.813 + .023 -
Microcline Heated	1.883 + .003 -	0.3403 + .0005 -	1.920 + .0032 -	5.693 + .032 -	0.767 + .003 -	0.414 + .0041 -	1.559 + .019 -
Plagioclase & Ser. Plag.	2.223 + .004 -	0.3257 + .0007 -	2.271 + .0043 -	7.232 + .035 -	0.709 + .002 -	0.434 + .0043 -	1.647 + .020 -
Plagioclase Heated	2.390 + .006 -	0.3148 + .0007 -	2.400 + .0063 -	7.849 + .041 -	0.704 + .003 -	0.341 + .0034 -	1.237 + .015 -
Ser. Plag. Heated	2.050 + .005 -	0.3321 + .0010 -	2.083 + .0054 -	6.381 + .037 -	0.716 + .003 -	0.409 + .0041 -	1.534 + .019 -
Apatite	2.89 + .02 -	0.291 + .003 -	2.89 + .022 -	10.46 + .12 -	0.7025 + .003 -		
Apatite Heated	2.60 + .02 -	0.305 + .004 -	2.60 + .023 -	8.86 + .12 -	0.7155 + .002 -		
Leach Heated	2659 + .00065 -	0.566 + .001 -	2.629 + .023 -	0.1321 + .0044 -	1.09 + .093 -		

Therefore, an estimate of the effect of the instrumental mass discrimination and its contribution to the error was made from previous runs of rubidium of known composition. There appeared to be no bias in the mass discrimination effect though an error of one percent was attached to the Rb^{85}/Rb^{87} ratio as a result of fluctuation in the instrumental mass discrimination. Peak height ratios for the rubidium isotopes were taken near the beginning of the runs where the ratio has changed least through the residual enrichment of the heavier isotope.

Error contributions were combined according to the expressions for combining standard errors in a compound quantity (Topping, 1955). Errors on normal strontium and rubidium were calculated according to Long (1963). From the expression giving normal rubidium and strontium, partial differentials were taken with respect to the measured ratio of non-spiked to spiked isotope to the amount of spike and to the fractions of the isotopes in the spike. For convenience, the expressions were given in weights and weight ratios. Thus the expression

$$N = -S \frac{RC'_N - Cs}{RC'_N - C_N},$$

where N = the weight of the normal element

R = the weight ratio of unspiked to spiked isotope

C_s, C'_s = the weight fractions of the unspiked and spiked isotope respectively in the spike

C_N, C'_N = weight fractions of the unspiked and the spiked isotope respectively in the normal element

S = the weight of the spike

yields by partial differentiation the error contribution to the normal element from the error in the determined isotope ratio:

$$\Delta N = \Delta R \frac{N}{R} \left[\frac{RC'_s}{RC'_s - Cs} - \frac{RC'_N}{RC'_N - C_N} \right]$$

similarly, from the error in the weight of the spike:

$$\Delta N = \Delta S \left[\frac{RC's - Cs}{RC'N - CN} \right]$$

from the error in the weight fraction of the unspiked isotope in the spike:

$$\Delta N = \Delta C_s \left[\frac{s}{RC'N - CN} \right]$$

and from the error in the weight fraction of the spiked isotope in the spike:

$$\Delta N = \Delta C_s \left[\frac{-SR}{RC'N - CN} \right]$$

Error contributions to the weight of normal strontium were combined and proportional errors calculated for the original strontium and Sr^{86} content of the rock phases. The error on the radiogenic strontium was calculated by combining the error on the Sr^{86} content with the error on the Sr^{87}/Sr^{86} corrected ratio.

Proportional errors were also calculated for the normal rubidium and Rb^{87} content of the rock phases, and the errors on the Sr^{86} and Rb^{87} contents were combined to give the error on the Rb^{87}/Sr^{86} ratio.

The error contribution of the measured Sr^{87}/Sr^{86} ratio in the spiked strontium to the radiogenic strontium can be calculated by partial differentiation of the expression for the radiogenic strontium content (Long, 1963):

$$\Delta X = \Delta R' [C's S + C'N N]$$

where ΔX is the error in the radiogenic strontium and $\Delta R'$ is the error in the mass spectrometrically determined ratio of Sr^{87}/Sr^{86} . The error for the Sr^{87}/Sr^{86} ratio of the leach was then calculated by combining the error on the Sr^{86} content with the error on the Sr^{87} content (which is obtained by combining the error on original Sr^{87} with that of radiogenic Sr^{87}).

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